On the Use of Partly Neutralised Mixtures of Acids as Hydrion Regulators.

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When mixtures of standard ($H^\cdot$) are prepared, as is usual, from partly neutralised acids, it is well known that the most suitable degree of neutralisation is that at which ($H^\cdot$) = k, the ionisation constant of the acid. This part of the neutralisation curve (ordinates, $-\log(H^\cdot)$ or $p_{H^\cdot}$; abscissæ, equivalents or number of c.c. of alkali) is approximately a straight line inclined at a relatively small angle to the axis of abscissæ. In the case of a dibasic acid there are two such regions corresponding to the first and second constants k_1 and k_2. Each of these flat parts of the curves covers a range of about 2 in $p_{H^\cdot}$. The intermediate parts of the curves (at which the differential increases, reaches a maximum, and then decreases) lie on each side of the points at which ($H^\cdot$) = $\sqrt{k_1 k_2}$. These inflections on the curves are less suitable, or may be quite unsuitable, for hydrion regulators if the ratio between k_1 and k_2 is about 10^3 or a still higher power.

If the constants do not bear a high ratio to one another, as in the case of citric acid ($k_1 = 8 \cdot 2 \times 10^{-4}$, $k_2 = 3 \cdot 2 \times 10^{-5}$, $k_3 = 7 \times 10^{-7}$), the curve of neutralisation will have no marked inflection throughout its course. The range of regulators obtained from citric acid, with the addition of HCl on the acid side, is unusually great (from $p_{H^\cdot} = 1$ to $p_{H^\cdot} = 6$). But other regulator mixtures—phosphates, borates, etc.—have marked inflections, and consequently several must be used if a wide range of ($H^\cdot$) is required. Also there is a small interval, between $p_{H^\cdot}$ = about 7·5 and 8·3, which cannot be reproduced from any of the standard mixtures with as high an accuracy as can be obtained at all other values of ($H^\cdot$). This interval happens to be that which has a particular importance in the measurement of the acidity of sea-water. These defects in existing standards would appear to be easily remediable by using a selected mixture of acids. For, if in the case of a polybasic acid k_1 bears too high a ratio to k_2, it should only be necessary to introduce another acid for which $k_3 = \sqrt{k_1 k_2}$ in order to flatten out the inflection and make this part of the curve also available. A number of acids could be chosen of which the constants differ by only 1 power of 10—*e.g.*, salicylic, $k = 1 \times 10^{-3}$; lactic, $k = 1 \cdot 35 \times 10^{-4}$; acetic, $k = 1 \cdot 8 \times 10^{-5}$. This mixture should give a neutralisation curve which should be almost linear over a limited range.

The need for new mixtures of this sort is, however, much less than that for a mixture of only two solutions which shall give the whole range required in practice with a moderate accuracy sufficient for colorimetric purposes.

Since there is only a negligible inflection when k_1/k_2, etc., are not more than 100, five acids should suffice to give the range from $p_{H^\cdot} = 2$ to $p_{H^\cdot} = 12$. Unfortunately a series of acids with the required constants accurately graded is difficult to obtain, and practically the choice is restricted to acids which fall far short of perfection in this respect.

A mixture of phosphoric, acetic, and boric acids was found to be suitable.

A solution which is n molar with respect to each of these may be considered as one which is n normal with respect to each of five monobasic acids with constants equal to k_1 (phosphoric), k acetic, k_2 phosphoric, k boric, and k_3 phosphoric.

Experimental.—The recrystallised boric acid (0·04 mol.) was dissolved in a part of the water (free from CO_2). Approximately molar solutions of the acetic and phosphoric acids were standardised against alkali free from carbonate. A volume of acetic acid equivalent to 20 c.c. of normal alkali, and a volume of phosphoric equivalent to 60 c.c. of normal alkali, were added to the boric acid,* and the whole made up to 500 c.c. Of this acid mixture 25 c.c. were mixed with 5, 10, etc., up to 25 c.c. of 0·2 N alkali, and made up to 50.

The $p_{H^\cdot}$ values of this 0·1 N acid at different degrees of neutralisation were determined with an electrode of large surface which had been used on many previous occasions. Diffusion potentials were reduced to low values by saturated KCl solutions. The correctness of the potentials was checked by preliminary measurements of the known combinations

(1) H_2Pt standard acetate | Saturated KCl | N/10 KCl HgCl Hg.
(2) H_2Pt standard acetate | Saturated KCl | Saturated KCl HgCl Hg.

The standard acetate (0·1 N with respect to both acetic acid and sodium acetate) was made from acetic acid and standard sodium hydroxide.†

A thermostat was not employed, but corrections were introduced where necessary for changes of temperature.

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* In the first series in the Table the alkali was 0·198 N, the acetic acid of corresponding strength, and the boric and phosphoric each 0·04 molar. In the second series the alkali was 0·198 N and the acids 0·198/5 molar, except the boric, which was 0·04 molar. The two series showed no differences greater than the experimental error of the measurements of E.M.F.

† See Walpole, 'J. Chem. Soc.,' vol. 105, p. 2509 (1914).

(1) At 18° E.M.F. observed = 0·6046, standard = 0·6046.
(1) At 14° „ „ = 0·6008 „ = 0·6017.
(2) At 14° „ „ = 0·5176 „ = 0·5169.

The regulator mixtures were then substituted for the standard acetate, and the E.M.F.'s determined in most cases of the decinormal calomel, and in some cases of the saturated calomel, combination.

The values of $-\log(\mathrm{H}^{\cdot})$ calculated from each kind of measurement of the same regulator mixture by the respective formulæ

$$p_{\mathrm{H}^{\cdot}} = \frac{\mathrm{E}-0{\cdot}338}{0{\cdot}0001983\,\mathrm{T}} \quad \text{and} \quad p_{\mathrm{H}^{\cdot}} = \frac{\mathrm{E}-0{\cdot}2509}{0{\cdot}0001983\,\mathrm{T}},$$

did not differ by more than 0·04 in $p_{\mathrm{H}^{\cdot}}$.

Some values of $(\mathrm{H}^{\cdot})$ were also checked by colour matching against the Sörensen standards.

R = percentage of neutralisation.	Indicator.	Standard solution to match.	$p_{\mathrm{H}^{\cdot}}$ of standard.
4	Methyl violet......	$\left\{\begin{matrix}\text{Citrate} & 3{\cdot}36 \\ \mathrm{HCl} & 6{\cdot}64\end{matrix}\right\}$	2·30.
40	Cochineal	$\left\{\begin{matrix}\text{Citrate} & 7{\cdot}48 \\ \mathrm{NaOH} & 2{\cdot}52\end{matrix}\right\}$	5·44.
92	Alizarin	2·56 equivalents of NaOH to 1 mol. of 0·1 molar H_3PO_4.	11·5 (from neutralisation curve of 0·1 molar H_3PO_4).

The agreement of these values (⊕ on the diagram) with the electrometric is as good as can be expected, considering that the limit of accuracy of a colorimetric match in test-tubes is 0·1 in $p_{\mathrm{H}^{\cdot}}$.

The electrometric values are given in the Table on p. 466 and in the diagram on p. 467.

The neutralisation curve based on these results is seen to have the character which could be foretold from the constants, etc.

Steps of $(\mathrm{H}^{\cdot})$......	H_3PO_4	CH_3COOH	H_2PO_4'	H_3BO_3	HPO_4''.
C of each = 0·04.					
k	$1{\cdot}1 \times 10^{-2}$	$1{\cdot}8 \times 10^{-5}$	2×10^{-7}	1×10^{-9}	3×10^{-12}
$-\log k$	1·96	4·745	6·70	9·0	11·523
$-\left(\frac{\log k_1 + \log k_2}{2}\right)$	3·352	5·722	78·50	10·26	

Percentage of total acid neutralised (R).	E.M.F. observed at $t = 14$–19^{c} (E_t).	$p_{H^\cdot} = (E_t - E_0)/0{\cdot}0_3198\,T$. $E_0 = 0{\cdot}338$ or $0{\cdot}2509$.
	First Series.	
0	0·446	1·88
4	$0{\cdot}462_5$	$2{\cdot}16_5$
10	0·475	2·38
20	0·533	3·39
24	0·568	4·00
28	0·588	4·35
30	0·603	4·60
40	0·664	5·71
50	$0{\cdot}732_5$	6·87
60	0·795	7·97
70	0·860	9·11
80	0·921	10·17
90	1·002	11·57
100	1·03	12·02
	Second Series.	
50 (decinormal KCl calomel)	$0{\cdot}731_5$	6·78
88 ,, ,,	$0{\cdot}990_5$	11·23
95 ,, ,,	1·015	11·75
50 (saturated KCl calomel)	$0{\cdot}645_5$	6·82
88 ,, ,,	0·902	11·25
95 ,, ,,	$0{\cdot}926_5$	11·75

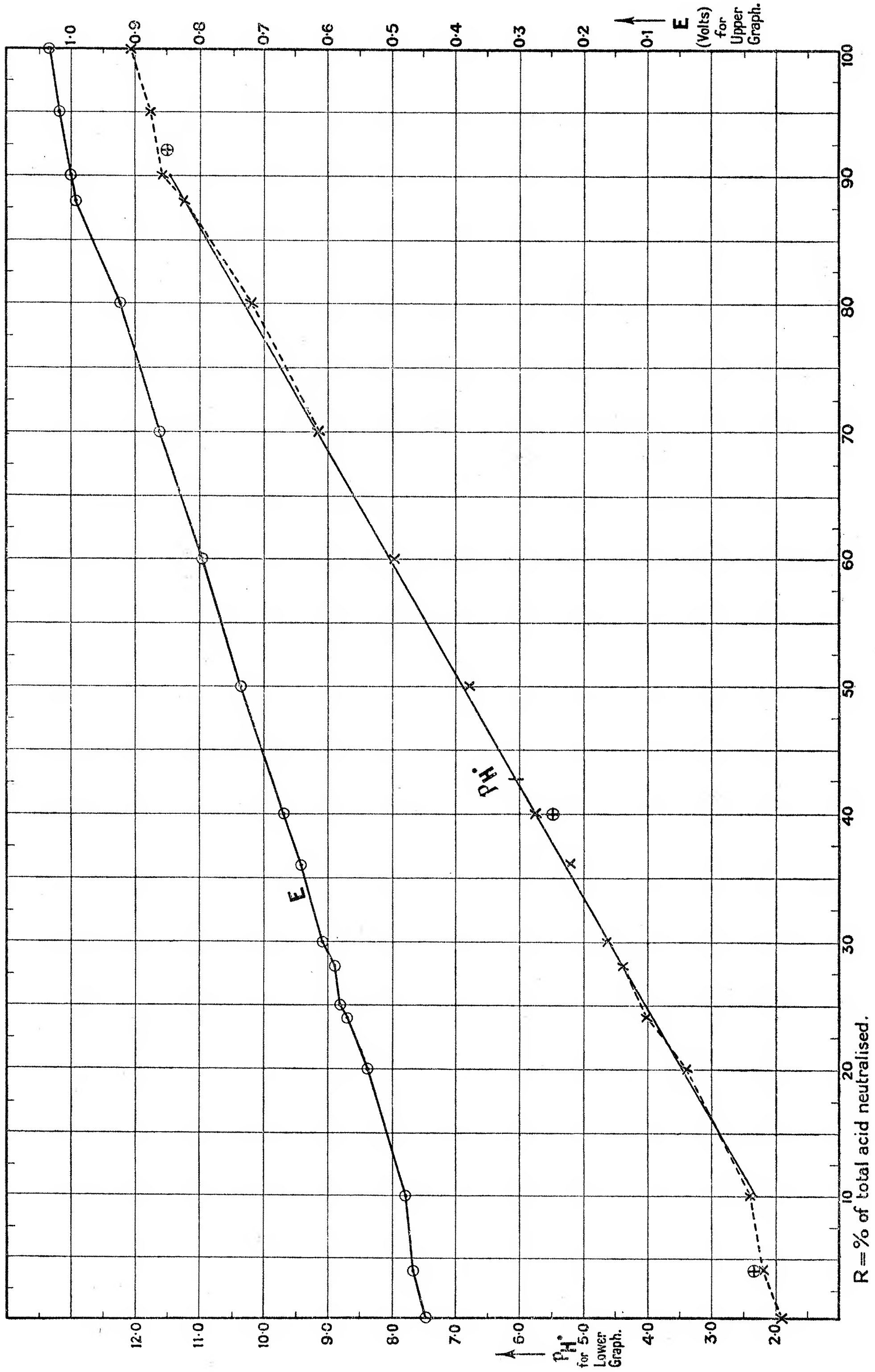
Any inflections remaining in the neutralisation curve should be found at values of $p_{H^\cdot}$ given by the figures of the lowest row, more especially at the first and last of these, which correspond to rather a high ratio k_1/k_2. Actually it is seen from the diagram that there are changes of curvature in the intervals which have their centres at about 3·5 and 10·5 than in the parts on either side of these intervals.

The whole central part of the curve can be expressed very well within the limits of accuracy of a colorimeter match (see p. 465 above) by the linear formula

$$p_{H^\cdot} = 2{\cdot}3 + (R - 10)\,0{\cdot}1144,$$

in which R has the meaning already given in the Table, and $= 4x$, where x is the number of cubic centimetres of 0·2 N alkali added to 25 of 0·2 N acid, and made up to 50. The formula holds up to $R = 90$, $p_{H^\cdot} = 11{\cdot}45$, and the values derived from it are not more than 0·15 in $p_{H^\cdot}$ from the experimental values, and usually within 0·1.

This empirical linear equation together with two others—one from $p_{H^\cdot} =$ 1·88 to 2·38, and another from $p_{H^\cdot} = 11{\cdot}45$ to 12·02—will express the whole range with sufficient accuracy for many purposes. Theoretical neutralisation curves may also be derived, based upon the successive


1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
E (Volts) for Upper Graph.
12·0
11·0
10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
$P_H^{\cdot}$ for Lower Graph.
10
20
30
40
50
60
70
80
90
100
R = % of total acid neutralised.
E
$P_H^{\cdot}$

constants k_1 and k_2, k_2 and k_3, etc., and the general equations 3*a* and 3*b* for dibasic acids.*

If the degrees of dissociation α, etc., of the sodium salts are taken as 1, the theoretical curve lies close to that found over all the middle part of the curve. But in absence of an independent knowledge of α, etc., these values will not be stated.

The practical advantages of these regulator mixtures over those previously proposed have been given as the objects of this investigation. The curve is suitable over the entire range from $p_{H^\cdot} = 2$ to nearly 12 if graphical methods are used. The middle part may also be expressed by a simple formula which includes all those values of $(H^\cdot)$ for which regulator mixtures are most needed. The interval from 7·5 to 8·3 is as easy to reproduce with accuracy as any other part. It may, perhaps, be suggested here that if this interval is required for determining the $(H^\cdot)$ of sea-water, etc., it may also be reproduced with accuracy by mixing equal volumes of "borate" and "secondary sodium phosphate" (Sörensen's standards), or of one-tenth molar borax and one-tenth molar Na_2HPO_4, which are nearly isohydric, and adding to the mixture the necessary amounts of HCl or NaOH (Sörensen). The inflection in the phosphate curve will thus be effectually flattened out. This and other mixtures which use the principle of intermediate constants will, of course, require to be standardised by the hydrogen electrode.

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* 'Roy. Soc. Proc.,' A, vol. 91, p. 537 (1915).